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Title: Adhesion of Titanium Coatings on Additively Manufactured Stainless Steel

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# Adhesion of Titanium Coatings on Additively Manufactured Stainless Steel

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MPA-11: Students: Charles Beauvais and Nicholas Bittner, Mentors: Tommy Rockward and Christopher Wetteland

## Introduction

The ongoing global climate change crisis has brought attention to the urgent need to reduce greenhouse gas emissions from vehicles by providing alternative zero-emission fueling technologies. Prevailing vehicles are dependent on fossil fuels and contribute to climate change by creating emissions of carbon dioxide. In 2019, transportation was the largest contributing economic sector to the U.S. greenhouse gas emissions total at 29% [1]. By converting vehicle fueling to an alternative method, major reductions in greenhouse gas emissions can be achieved. Hydrogen fuel cells are one potential alternative capable of generating electricity from hydrogen while emitting only water. Several obstacles hinder the development of hydrogen fuel cells as a viable alternative, including the manufacturability of bipolar plates.

Additive manufacturing, otherwise known as 3D-printing, is considered to be a noteworthy manufacturing option with the potential to expedite fuel cell development, reduce manufacturing waste, and enable revolutionary designs not otherwise possible [2]. Typical subtractive manufacturing fabricates parts by carving the design out of a large portion of source material while accumulating wasted excess material which must either be recycled or discarded. This method also often limits designs to what can be fabricated externally by the manufacturing tool. Additive manufacturing stands in contrast to subtractive manufacturing by fabricating parts by addition of material rather than removal. Additive manufacturing reduces wasted material by only consuming material which becomes part of the fabricated item. The common layer-by-layer additive manufacturing process offers greater freedom of fabrication throughout the body of the part, thereby permitting more elaborate fuel cell designs.

During fuel cell operation, bipolar plates are exposed to corrosive conditions, which makes protective coatings an important element to include. The application of protective coatings to parts made by the emerging technique of additive manufacturing requires special attention. Additively manufactured parts often feature rough exteriors which can be detrimental to coating adhesion. Corrosion and prevention coatings for additively manufactured parts and the effects of surface roughness on coating adhesion are the main topic of this summer internship project.

For this project, summer interns from MPA-11 and MST-7 collaborated to improve adhesion of titanium films on AM 316L stainless steel substrates by methods of grinding, polishing, solvent cleaning, remote plasma cleaning, and titanium physical vapor deposition. The two groups were particularly interested on the influence of surface roughness on the adhesion strength of a titanium protective coating. Students Charles Beauvais and Nicholas Bittner worked with MPA-11 to

additively manufacture stainless steel samples, mount them for polishing, and grind and polish them to various roughness levels. They worked from Navajo Technical University while also participating as mentors to students of the university. I, Isaac Stricklin, worked with MST-7 to characterize the roughness levels of the stainless steel pucks, clean them by use of solvents and plasma cleaning, deposit titanium coatings, and characterize the adhesion strength of the titanium film. This report details the progress made by the students and the results of their efforts.

## Experiment

The process was initiated by Charles and Nick of MPA-11 with the fabrication of a batch of eight stainless steel samples by directed-energy deposition (DED) additive manufacturing using stainless steel 316L powder source material. The parts were manufactured within an argon environment to prevent inadvertent reactions taking place during printing.

After fabrication, Charles and Nick prepared the samples for grinding and polishing by compression mounting the samples in glass-reinforced epoxy resin mounts. Compression mounting took place at a temperature of 200°C. The mounts provided a larger mass for the polisher to hold the samples.

After mounting, the samples were grouped into two sets of four samples with each sample within a set receiving a mechanical surface smoothening treatment. Three samples within each set were ground and grit polished to three different final grit levels of 360, 600, or 1200. The fourth sample within each set underwent surface leveling conducted by milling followed by bead blasting at MST-7 by Douglas Vodnik. Following all preparations, the samples were transferred to MST-7 for the next steps in the process.

Upon receipt of the samples, Isaac Stricklin and Douglas Vodnik of MST-7 began their part of the process with pre-deposition characterization of the samples. An IR microscope was used to acquire images of surface quality before deposition. A Scanning Electron Microscope with Energy-dispersive X-ray spectroscopy capabilities was used by Alex Edgar of MST-7 to analyze the surface of a stainless steel sample. The analysis detected elements typical of 316L steel such as iron, chromium, nickel and molybdenum. A carbon-rich region was also detected, confirming the importance of contamination cleaning for the samples.

Next, stylus profilometry was used to measure profile and surface roughness of the samples. Measurements took place near the center of each sample, using a tip with stylus radius 12.5  $\mu\text{m}$ , with scan lengths of 5000  $\mu\text{m}$ , stylus force of 3 mg, and a vertical scan range of 6.5  $\mu\text{m}$ . Due to the printing technique of fabrication and circular method of polishing, directional textures were observed on the surfaces of the samples. For that reason, scans were done in two perpendicular directions on each sample, one scan parallel with the printing direction and another perpendicular to the printing direction. In addition, some samples exhibited curved profiles. For that reason, RMS roughness values were calculated over relatively linear regions of the profile to avoid areas under profile curvature from contributing to the roughness calculations.

Following pre-deposition characterization, the eight samples were prepared for titanium physical vapor deposition. Solvent cleaning within an ultrasonic bath was performed on each sample for

degreasing and to remove loosely adhered contamination. Solvent cleaning was performed by Victor Siller and Isaac Stricklin of MST-7. Each sample was immersed in acetone for 30 minutes, followed by methanol for 30 minutes, finishing with immersion in deionized water for 30 minutes. Samples were not scrubbed or wiped to avoid further scratching, polishing, or other modification to the surface quality.

From there, each set of samples was loaded into its respective deposition chamber. Set 1 was loaded into the electron beam physical vapor deposition chamber. Set 2 was loaded into the sputter deposition chamber. With the samples loaded, a PIE Scientific EM-KLEEN plasma cleaner was used to apply remote plasma cleaning treatments to each sample. Plasma treatments are often used to remove hydrocarbon and other contaminants and are known to improve adhesion strengths of films when performed before deposition [3]. The plasma treatment was conducted for a duration of 5 minutes using air as the process gas, plasma source pressure of 51.2 mTorr, RF Forward power of 75 W, RF reverse power of 1 W, and temperature of 26.5°C. Upon completion of remote plasma cleaning, the chambers were put under high vacuum.

Set 1 of the samples received a titanium coating provided by electron beam physical vapor deposition. Electron beam evaporation deposition is a common technique that is simple to execute, can provide high deposition rates, and makes use of sources in easily accessible forms, such as chunks of the material [4]. Deposition was performed with base pressure of 1E-7 torr and accelerating voltage of 10kV. Deposition rates varied throughout the process, beginning with 0.5 Å/s for the first 500 Å, 1 Å/s for the next 500 Å, with a final deposition rate of 5 Å/s. The slow initial deposition and quicker final deposition were used to provide a thorough coating at the steel/Ti interface while keeping the total deposition time practical. The total coating thickness was approximately 10,870 Å as verified by profilometry performed on a silicon witness sample which was loaded with the stainless steel samples.

Set 2 of the samples received a titanium coating provided by magnetron sputtering physical vapor deposition. Magnetron sputtering deposition is a recognized for its capability of forming dense films with quality adhesion [5]. Deposition took place with argon as the process gas, a process pressure of 2E-3 torr, argon flow rate of 10 sccm, DC Power of 150 W, and deposition rate of 5 Å/s. The total coating thickness was approximately 10,930 Å as verified by profilometry performed on a silicon witness sample which was loaded with the stainless steel samples.

Following deposition, all 8 samples were simultaneously prepared for stud pull adhesion tests. Preparation was done by attaching an epoxy-coated test stud to the films of the samples and placing them into an oven at 150°C for 1 hour to bond the epoxy to the films. The samples with attached studs were then allowed to cool. From there, the adhesion test was performed using a ROMULUS Universal Mechanical Strength Tester equipped with a Pull Down Breaking Point Module [6]. The adhesion tester operates by the stud pull adhesion test method by which a stud of known surface area with a high-strength adhesive is adhered to the film. The tool pulls the stud away from the sample with increasing force until the stud is removed due to the film failing or the adhesive epoxy of the stud failing. The epoxy has an adhesion strength rating of 10,000 PSI [6]. The adhesive strength of the film is calculated by the force at breaking point divided by face area of the stud.

After the adhesion tests, another set of inspection measurements were made. Stylus profilometry scans were performed using the same parameters as before to evaluate changes in roughness after titanium deposition. Infrared microscopy images were taken as well with focus on the test site of the stud pull adhesion test. Results

Overall, each of the results of characterization measurements performed present a positive outcome. Figure 1 shows the IR microscope images of the 6 grit polished samples. The images show a clear and consistent smoothening of the stainless steel surfaces. As would be expected, the samples polished by higher grit showed smoother surfaces than lower grit samples. There were no apparent undesirable effects owing to the additive manufactured origin of the samples, such as porosity or granularity in the surface. The polished surfaces are revealed by the images to have excellent density and smoothness.

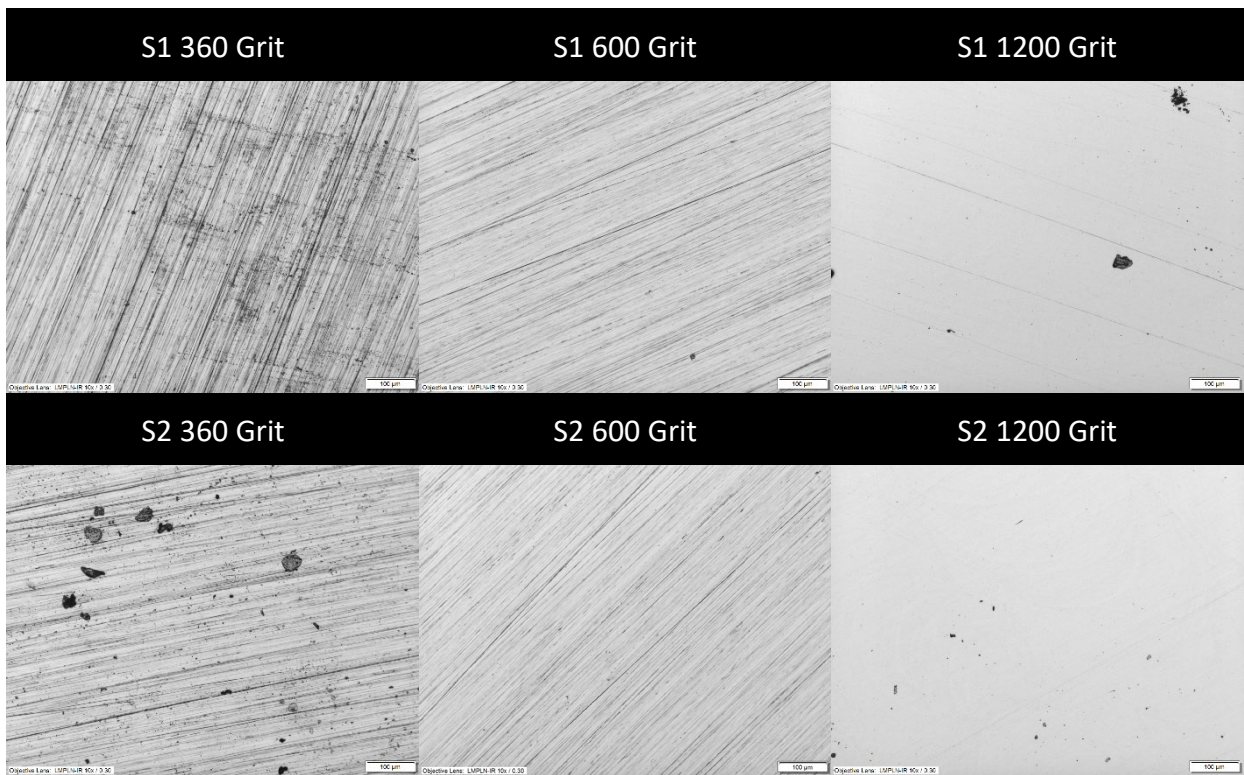


Figure 1: IR microscopy images of the 6 grit-polished samples.

The RMS roughness values of the surfaces of each sample are given in Table 1 and Table 2. Table 1 presents the roughness values of the stainless steel substrates before titanium deposition while Table 2 presents the roughness values of the titanium surface after deposition. The smoothening of the surfaces that was visible in the microscope images is also seen in the profilometry scan roughness values. The milled and bead blasted samples had the highest roughness levels with values on the order of 2000 or 3000 nanometers. As might be expected, the 1200 grit-polished samples displayed the lowest roughness with values of tens of nanometers. While there was a visible difference in surface texture by direction during image, the RMS roughness values do not show an appreciable difference in roughness values by direction. The RMS roughness values of

the titanium surfaces after deposition are presented in Table 2. The post-deposition roughness values are generally higher in comparison to the pre-deposition values.

	Measured Along Print Direction				Measured Across Print Direction			
	Milling and Bead Blasting	360 Grit	600 Grit	1200 Grit	Milling and Bead Blasting	360 Grit	600 Grit	1200 Grit
<b>S1: E-beam Coating</b>	2410.7 nm	42.1 nm	20.02 nm	10.3 nm	2588.43 nm	34.92 nm	17.39 nm	15.08 nm
<b>S2: Sputter Coating</b>	3437.46 nm	84.03 nm	22.96 nm	3.92 nm	3832.64 nm	45.82 nm	16.68 nm	13.57 nm

Table 1: RMS roughness values of surfaces before deposition

	Measured Along Print Direction				Measured Across Print Direction			
	Milling and Bead Blasting	360 Grit	600 Grit	1200 Grit	Milling and Bead Blasting	360 Grit	600 Grit	1200 Grit
<b>S1: E-beam Coating</b>	3378.3 nm	231.69 nm	297.64 nm	189.16 nm	2594.49 nm	69.17 nm	17.41 nm	109.76 nm
<b>S2: Sputter Coating</b>	4516.92 nm	97.35 nm	46.93 nm	34.86 nm	3355.25 nm	40.98 nm	23.76 nm	35.93 nm

Table 2: RMS roughness values of surfaces after deposition

An early pair of practice adhesions tests were performed on 2 samples that were not part of the main adhesion experiment. While these practice tests were intended to test the viability of the test process to the AM stainless steel samples, their results shown in Figure 2 nonetheless provided useful information. The dotted red line in the figure delineates the maximum strength rating of the test stud epoxy, which is taken to be the upper limit to strengths which the tool can test. This pair of samples were epoxy-mounted, grit-polished, and coated with 0.5  $\mu\text{m}$  of titanium. The samples were coated in the state as received by MST-7 without solvent cleaning or plasma cleaning before deposition. The stud pull adhesion tests showed relatively low film adhesion strengths of 272 and 1765 PSI. The tests performed in the main experiment showed better results.

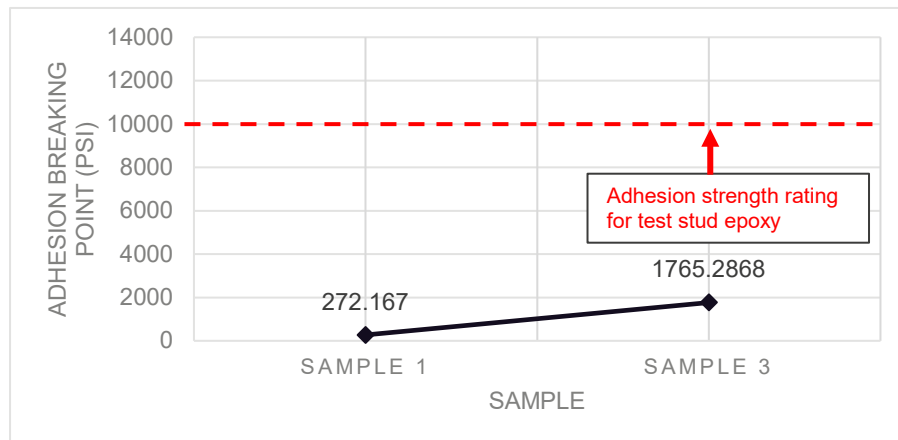


Figure 2: Film adhesion strengths of two practice samples.

The adhesion strength measurements of the main experiment are displayed in Figure 3. The results show that 7 out of 8 coatings had very high adhesion strengths in the range of 9400 PSI to 12,600 PSI, with the adhesion breaking point of each being near or above the adhesion strength rating of the test stud epoxy. Taking into consideration performance variations of the test stud epoxy and microscope images to be shown further on, it is believed that these 7 samples had coatings which outperformed the test stud epoxy. In that event, the coating adhesion strengths could potentially be higher than the values measured from the test and alternative adhesion measurement methods might be necessary to more thoroughly determine differences in film adhesion between preparation methods. Nevertheless, the values show that all film coating preparation methods used can provide high adhesion in titanium coatings. No apparent difference in adhesion strength was seen between surface smoothening and titanium deposition techniques.

The single sample which did not exhibit a strongly adhesive coating was the sample which received milling and bead blasting treatment as well as a sputter coating. This sample displayed the lowest adhesion strength at 6,900 PSI. However, during the measurement of this sample, I unfortunately did not mount this sample securely enough, so the stud slipped out of grip of the tester and this sample was tested 3 times before the breaking point was reached. It is possible that these successive tests weakened the film prematurely and gave rise to the lower adhesion strength value. Therefore, the adhesion strength of that value should be taken with caution and further measurements would be needed for a more definitive result.

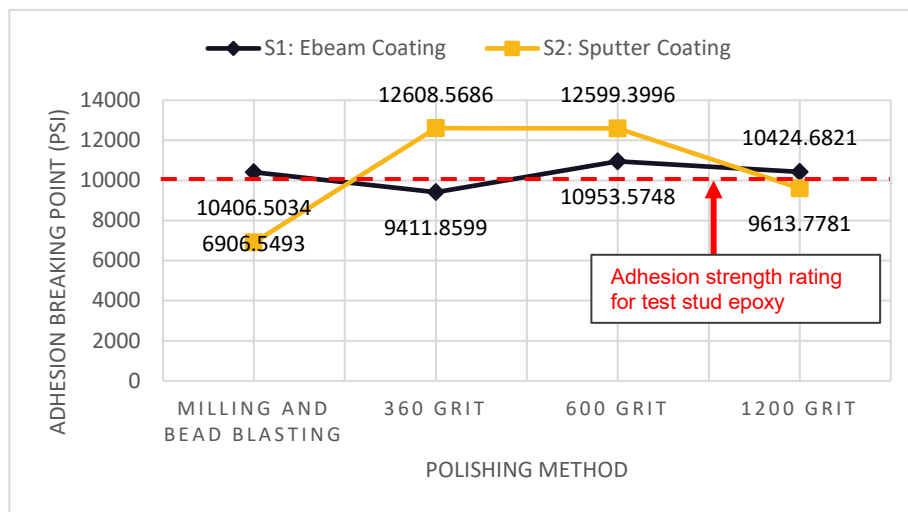


Figure 3: Film adhesions strengths of 8 samples with various surface smoothening and coating deposition techniques.

Microscope images in of the adhesion test sites, shown in Figure 4, provide further insight into the adhesion test measurements. In all 8 of the samples, portions of the epoxy from the test stud remain on the surface. This observation, in combination with the measured adhesion strengths being near the maximum rating of the test studs, suggests that the epoxies of the test studs suffered partial failure and were partially responsible for the adhesion breaking. However, some titanium coating was removed from most samples during the course of testing, suggesting there was partial failure of the film coatings as well. The milled and bead blasted samples showed areas of titanium coating larger than the other samples, which possibly indicates weaker adhesion. However, more definitive



measurements would be needed to verify. The other six samples showed smaller regions or no regions of titanium removed. In those cases, it should be cautioned that the adhesion strengths are calculated as force per unit area, with the area assumed to be the area of the stud. The removed areas of titanium smaller than the stud were likely subject to higher forces per unit area than measured by the tool. Therefore it should be considered that the film adhesion strength values measured and calculated by the tool might not be the exact failure points but lower bounds on the values.



Figure 4: 10x microscope images of the stud pull adhesion test sites. The remains of the test stud epoxies are visible as black circles.

## Conclusion

A sample preparation process implementing surface smoothening, plasma cleaning and physical vapor deposition was successfully developed for producing high-adhesion titanium coatings onto additively manufactured stainless steel samples. 7 out of 8 samples exhibited titanium adhesion strengths of 9,400 - 12,600 PSI, likely breaching the approximate 10,000 PSI test limit of the adhesion pull tester. Adhesion in those 7 samples showed no apparent difference based whether surface smoothening was done by milling and bead blasting, by low grit count polishing, or by high grit count polishing. In addition, adhesion in those 7 samples also showed no apparent difference based on whether magnetron sputtering deposition or electron beam evaporative deposition was used to deposit the titanium coatings. The sample prepared by milling and beading and coated by magnetron sputter coating showed a weaker adhesion of 6,900 PSI, however this may be due to operator error on my part and a more clear tests would be needed to confirm adhesion strength. Overall, all preparation and deposition techniques are viable candidates for a high-adhesion titanium coating.

There are many future steps which can be taken for this work. More specific experiments could be conducted to determining the particular contribution of plasma cleaning to the film adhesion strength. Alternative adhesion tests, such as scratch adhesion tests, could be useful in further differentiating adhesion strengths between samples if higher adhesion is required. While air plasma

cleaning was part of this successful process, hydrogen/argon plasmas could be considered for more aggressive cleaning if needed. Corrosion resistance testing is an important next step to determine which of the preparation methods is most suitable for a corrosion resistant titanium coating. Currently, this work has shown that there are many viable options to be considered for titanium coating for additively manufactured stainless steel.

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